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Method and device for determination of the redox state of a reaction surface coated with a catalyst material

The invention relates to a method and device for determining the redox state of the anode of a high-temperature fuel cell, which is coated with or made from catalyst material, or of the reaction surface of a reformer, and further to a piezoelectric sensor device for determining the redox state of an oxidizable/reducible coating.

High-temperature fuel cells, such as e.g. the solid oxide fuel cell or the molten carbonate fuel cell, must be supplied with gases at the electrodes during operation, i.e. combustion gas (H_2, CO or CH_4) at the anode and oxidizing gas (O_2 or air) at the cathode. The gas spaces must be sealed against each other. Insufficient sealing results in a reduction of the cell voltage and usually leads to degradation and failure of the fuel cell.

In addition, if oxygen enters an H_2-enriched anode space at temperatures below 600°C, a highly explosive mixture will result.

Nickel (Ni) or nickel-cermet may be used as catalyst material at the anode, but this will form nickel oxide (NiO) in contact with an atmosphere containing oxygen, and its catalytic activity will deteriorate. For this reason starting the operation of a high-temperature fuel cell with Ni or Ni-cermet as anode material requires a so-called reduction phase during which the anode space is initially flushed with nitrogen and is then subjected to the combustion gas (e.g. hydrogen), which acts as reducing agent and whose concentration is increased in

a stepwise manner. During this reduction phase NiO is reduced to metallic Ni. Conversely, oxidation of the anode material cannot be avoided on certain occasions, e.g. during maintenance activities. Reduction and oxidation of the anode is referred to as the "redox cycle".

It is known practice to determine such redox cycles, or the redox state, of Ni/YsZ-cermet anodes (YsZ = yttrium doped zirkonium) via their polarisation state, for instance by impedance spectroscopy. This method is used primarily in the development of fuel cells, but reliable inferences regarding the catalytic activity of the anode are only possible in single cell experiments. The method is not suitable for continuous monitoring of high-temperature fuel cells during operation.

From "Kinetics of Oxidation and Reduction of Ni/YsZ Cermets", 5th European Solid Oxide Fuel Cell Forum, Vol. 1 (2002), pp. 467-474, authored by Daniel Fouquet, Axel C. Müller, André Weber, and Ellen Ivers-Tiffée, there have become known findings concerning the kinetics of the reduction and oxidation of NiO/Ni powder and NiO/Ni-YsZ cermets, obtained with the use of TGA measurements (Thermo Gravimetric Analysis). Measurements of this kind cannot be used for the continuous monitoring of high-temperature fuel cells, however.

Reformers, e.g. vapour reformers for the generation of hydrogen-rich combustion gas for fuel cells, have reaction surfaces coated with catalyst materials, at which a combustion gas containing H_2 and CO is obtained, for instance from the primary media natural gas and water vapour. Reformers working with methanol as a primary medium are also used to generate a hydrogen-rich combustion gas according to the equation

$$CH_3OH + H_2O + heat \rightarrow 3H_2 + CO_2$$

Different redox layers, e.g. Ni/NiO or nickel-cermet, are used as catalyst materials. Efficiency and operational safety of the reformer depend on the state of the reaction surface.

From U.S. Pat. No. 6,455.181 B1 a fuel cell assembly is known which has a sensor with a membrane electrode, whose one side is connected with the gas feed of the fuel cell and whose other side is connected with the exhaust of the fuel cell, the two sides having different coatings. The different composition of the gas on the two sides of the membrane, for instance a difference in hydrogen ion concentration, is converted into an electric signal, which can be used to control the gas flow of the fuel cell. Thus differences in the gas concentration at the inlet and the outlet of the fuel cell are measured, but the device cannot be used for determination of the redox state of the anode of a high-temperature fuel cell or the redox state of the reaction surface of a reformer.

It is the object of the present invention to propose a method and device as well as a sensor arrangement for the monitoring of the redox state of the anode of a high-temperature fuel cell or of the catalytic reaction surface of a reformer, which may be used during normal operation and which should furthermore ensure optimised and safe operation of the fuel cell or fuel cell assembly including the reformer, by controlling or adjusting at least one operational parameter.

The invention achieves its aim by providing that at least a first resonator of a piezoelectric sensor device is brought into contact with the anode gas flow containing H_2 and/or CO

and/or CH_4, of the high-temperature fuel cell, the surface of the first resonator being furnished with a coating which can be oxidized/reduced in the anode gas flow, and that at least one change in the resonance properties, preferably the resonance frequency, of the first resonator is measured and the redox state of the anode of the high-temperature fuel cell is inferred from this measurement.

For monitoring the reaction surface of a reformer the invention proposes that at least one first resonator of a piezoelectric sensor device be brought into contact with the gas flow of the reformer containing H_2 and/or CO and/or CH_4, the surface of the first resonator being provided with a coating that can be oxidized/reduced in the gas flow, and that at least one change in the resonance properties, preferably the resonance frequency, of the first resonator be measured and the redox state of the reaction surface of the reformer be inferred from this measurement.

A device according to the invention for implementing the method is characterised in that a first resonator of a piezoelectric sensor device is positioned in the anode gas flow of the high-temperature fuel cell or in the gas flow of the reformer, this first resonator being coated with an oxidizable/reducible layer, and that there is provided a unit for measuring at least one change of the resonance properties of the first resonator, the measured value being a measure for the redox state of the high-temperature fuel cell or a measure for the redox state of the reaction surface of the reformer.

In an advantageous variant of the invention the oxidizable/reducible coating of the first resonator is made from material identical with the catalyst material of the anode of the high-

temperature fuel cell or the catalyst material of the reaction surface of the reformer.

Free standard-formation-energy of oxides, which depends on temperature and partial pressure of oxygen, may be read off the so-called Ellingham diagram for oxides, which is of importance especially in the extraction of metals from oxides. Examples of oxidizable/reducible coatings of the first resonator (for gases containing CO and/or H_2 or CH_4) include Cu/CuO, Ni/NiO, Pb/PbO, Co/CoO, Ag/AgO, Pd/PdO and nickel-cermet).

For difference measurements the invention proposes that at least one second resonator of the piezoelectric sensor device be placed in the gas flow, this second resonator having a coating which is chemically stable in the gas flow. The frequency difference between the first and second resonator of the sensor device is used as a measure for the redox state of the oxidizable/reducible layer. Examples of chemically stable layers (for gases containing CO and/or H_2 or CH_4) are CaO, MgO, Al_2O_3, TiO_2, SiO_2, MnO, V/VO, Cr/CrO, and noble metals.

It is proposed by the invention that, depending on the measured change of resonance properties, preferably the change in resonance frequency, at least one operational parameter of the high-temperature fuel cell or the reformer be controlled or adjusted.

According to the invention further operational parameters may be obtained by measuring the resonance frequency or resonance resistance of one of the two resonators, preferably the resonator with the chemically stable coating, and by using the measured value as a measure for temperature or pressure in the

gas flow. From the data on temperature, pressure and redox state obtained at the measurement location the redox state of the anode may be found using pressure and temperature data from the anode space of a fuel cell. The device of the invention permits for instance control of the combustion gas supply or of the composition of the combustion gas at the anode and/or temperature control during the start and/or stop phase.

A piezoelectric sensor device for determination of the redox state of an oxidizable/reducible coating according to the invention is characterised in that the oxidizable/reducible coating is applied to the surface of at least one first resonator of the sensor device, the resonator surface being flow-connected to the anode gas space of a high-temperature fuel cell or the gas space of a reformer. Preferentially, a chemically stable coating is applied to the surface of at least one second resonator of the sensor device, which coating does not show any redox behaviour in the gas flow of the high-temperature fuel cell or of the reformer. Both resonators may preferably be configured as BAW- or SAW-resonators.

In a preferred application the piezoelectric sensor according to the invention can be used to detect oxygen leaking into the anode space, in particular during the critical start-up phase (e.g. from the cathode space), whereupon a switchoff or emergency shutdown procedure for the fuel cell assembly may be initiated.

The piezoelectric sensor device may be positioned on the inlet side or on the outlet side of the anode gas flow of the fuel cell. During normal operation of the fuel cell the gas

composition at the outlet of the fuel cell (e.g. CH_4, H_2, CO, CO_2, N_2, and H_2O) is temperature- and load-dependent.

In a variant of the invention the piezoelectric sensor device may also be placed in the anode gas space of the high-temperature fuel cell or on the outlet side of the gas flow from the reformer.

The invention will now be explained in more detail using the enclosed schematic drawings as reference.

Fig. 1 is a schematic view of the device of the invention for determining the redox state of the anode of a high-temperature fuel cell with the piezoelectric sensor according to the invention;

Fig. 2 is a variant of the device of fig. 1 in a fuel cell assembly with a vapour reformer.

Fig. 1 shows a device for determining the redox state of the anode 11, either coated with or consisting of a catalyst material, of a high-temperature fuel cell 10, where in the anode gas flow 5 containing H_2 and/or CO and/or CH_4 a piezoelectric sensor device 1 is located, whose first resonator 3 is furnished with a coating 4, which can be oxidized/reduced in the anode gas flow. The surface of the resonator is flow-connected to the anode gas space 11′ and, in the example shown, placed on the outlet side of the high-temperature fuel cell 10. The cathode of the fuel cell 10 is referred to as 12.

The sensor device 1 has a second resonator 6, whose surface is provided with a chemically stable, inert coating 7, which does not exhibit any redox behaviour in the anode gas flow 5 of the

high-temperature fuel cell 10. The second resonator 6 may for instance be coated with a noble metal or an inert oxide layer. The chemically stable coating 7 and the oxidizable/reducible coating 4 of resonators 3 and 6 may be applied onto two areas of a piezoelectric crystal element 2, as shown in fig. 1. Both resonators will thus have the same material-dependent parameters, making signal evaluation substantially easier.

If SAW-resonators are used, excitation of the resonators and signal pick-up may be carried out by wireless methods.

If the first resonator 3 is designed as a BAW-resonator, its opposing surfaces may each be coated with the oxidizable/ reducible coating 4, thereby achieving double signal intensity per mass.

It is furthermore possible to measure resonance frequency or resonance resistance by means of the resonator 6 with chemically stable coating 7, and to use the obtained value as a measure for temperature or pressure in the anode gas flow 5.

The device of fig. 1 is provided with a unit 8 for measuring at least one change of the resonance properties (e.g. resonance frequency) of the resonators 3 and 6 of the piezoelectric sensor device 1, the obtained value yielding a measure for the redox state of the anode 11 of the high-temperature fuel cell 10. Via a control unit 9 diverse operational parameters of the high-temperature fuel cell 10 may be controlled.

In fig. 2 a fuel cell assembly with a fuel cell 10 and a vapour reformer 13 running on natural gas is schematically shown. The piezoelectric sensor 1 described in fig. 1 may be

placed in the anode gas flow in front of the anode 11 of the fuel cell 10, respectively on the exit side of the gas flow from the reformer 13 (point A), and via the measurement data gathered it may provide information concerning the state of the anode 11 in the anode gas space 11' of the fuel cell 10, as well as the state of the reaction surface 16 in the gas space 13' of the reformer 13. The sensor device 1 could also be placed on the entry side of the reformer 13 (e.g. in a common feed line for natural gas and water vapour), or behind the anode 11 (point B), or also behind an optional heat exchanger 14 and in front of an afterburner 15 (point C).